CORNELL AERONAUTICAL LABORATORY, INC. Buffalo, New York

NONEQUILIBRIUM GASDYNAMICS RELATED TO PROPULSION SYSTEMS

Contract NASr-109 QUARTERLY REPORT FOR PERIOD ENDING 30 September 1965

1. INTRODUCTION

During the past quarter, the research performed under Nonequilibrium Gasdynamics, Contract NASr-109, has concentrated on the following areas:

- (1) Completion of a report on theoretical studies of catalysis of hydrogen-atom recombination,
- (2) Completion of a report on the machine computer code for the numerical solution of the inviscid streamtube flow of a reacting mixture.
- (3) Completion of three papers on expansion-flow studies, and further work on expansion flows by the line reversal method, and
- (4) Development and application of the technique of measuring atomic concentrations in shock-wave flows by absorption spectrophotometry,

The report on the theoretical gas-phase catalysis studies has been published. The report on the machine computer code has passed editorial review and is now being printed for issuance as a CAL report. Three papers 3-5 dealing with expansion-flow studies have been submitted for publication.

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2. THEORETICAL GAS-PHASE CATALYSIS STUDIES

The report on the theoretical gas-phase catalysis studies has been published. The contents and principal conclusions of this work have been discussed in the progress report of 31 March 1965. The most important conclusion concerns the saving in tankage weight that may be achieved by the use of catalytic additives of greater density than liquid hydrogen. In view of the great practical significance of this finding, some additional work on this aspect of the gas-phase catalysis problem will be carried out, and it is planned to publish the results in a technical note.

3. STREAMTUBE PROGRAM REPORT

The report on the computer program for the numerical solution of one-dimensional inviscid flows of multicomponent reacting mixtures² is being typed in final form after passing editorial review, and will be issued in the near future as a CAL report. A detailed outline of the report has been presented in the progress report of September 30, 1964.

4. SPECTRUM-LINE REVERSAL STUDIES

During the past quarter, three papers were submitted for publication in appropriate technical journals. The first paper is a revised version of one previously submitted to J. Chem. Phys. dealing with the line-reversal measurements in Ar expansion flows. The revisions consist mainly of including some discussion of the effect of possible self-absorption of the spontaneous Na emission on the inferred free-electron temperatures. In addition, some clarification is included of the mechanism by which the free-electron temperatures freeze at relatively high values. A discussion of these aspects is contained in the Quarterly Report for period ending 30 June 1965.

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The second paper⁴ is a technical note dealing with the influence of impurities on the Na-line reversal temperature measurements in N₂ expansion flows. The contents of this note have been briefly described in the Quarterly Report for period ending 31 March 1965. The note has been submitted for publication in the J. Chem. Phys.

The third paper⁵ is a brief summary of the previous results of measurements of nonequilibrium static pressures in dissociated-hydrogen nozzle flows⁶. The results support, within the accuracy of the measurements, the applicability of shock-wave dissociation-recombination data to the nozzle flow data. Moreover, these results illustrate the difficulty of obtaining accurate rate data from pressure measurements. This note has been submitted for publication in the AIAA Journal.

Also, during the past quarter, preliminary studies of the vibrational de-excitation of CO in expansion flows were initiated. The principal objectives of these studies are to obtain vibrational de-excitation rates for CO in the expansion flow environment and to compare these rates with available shock wave data. This comparison is of interest in view of previous work which had shown that N2 relaxes vibrationally in the nozzle flow at a rate which is much faster than the shock wave data would indicate 3,7. The comparison of relaxation rates is based on the applicability of the Landau-Teller theory to describe the relaxation process.

For these studies a test gas mixture of 5% CO + 95% Ar was used in order to provide a direct comparison with existing shock wave data⁸ for the same test gas composition. In the experiments carried out thus far, a reservoir pressure of about 45 atm and reservoir temperatures in the range

of 3600° K to 5200° K were employed. The Na line reversal technique was used to measure temperatures at a nozzle area ratio of $A/A^* = 8$.

The preliminary analysis of the data was based on the assumption that the line-reversal temperature was equilibrated with the CO vibrational temperature only. This correspondence may not be completely valid since the electrons arising from Na ionization in the reservoir have a large cross section for Na excitation. Also, due to the low Na ionization potential of about 5.1 ev the number density of electrons at the high reservoir temperatures may be large. In this respect, the analysis may be somewhat conservative.

The data obtained so far from the experiments clearly indicate temperatures considerably lower, i.e., closer to equilibrium, than the temperatures computed on the basis of the Landau-Teller theory with shock wave data. Within the framework of the Landau-Teller theory, these results imply de-excitation rates for CO vibration between one and two orders of magnitude faster than the shock wave data. This result is consistent with the previous N₂ results and suggests that the faster rate of vibrational de-excitation in comparison with shock wave excitation is not a peculiarity of N₂ but rather may be characteristic of other molecules as well.

5. ATOMIC SPECTROPHOTOMETRIC STUDIES

Measurements of the rate of formation of atomic hydrogen behind incident shock waves have been continued in the high-purity shock tube. A large number of experiments have been completed for mixtures of 10% hydrogen in argon. The temperature range covered was 1700°-2400° K at pressures between 0.8 and 2.7 atmospheres behind the shock. The

experimental data were found to be very reproducible and the scatter on a plot of log k_{dissoc}, against the reciprocal of temperature was very small. These dissociation rate constants, which are determined from the initial portion of the absorption data where any gas-phase catalytic effect would be most important, are approximately 100 times slower (at 3000° K) than any data previously published.

A series of experiments using 1% hydrogen in argon is now under way, and the first few results indicate very good agreement with the data obtained for 10% hydrogen in argon. The temperature scale covered in this series will extend upwards from 2200° K.

The tube has not yet been baked and these experiments have been made under conditions of a vacuum of 3-4 x 10^{-7} mm Hg and leak rates of approximately $1\mu/200$ minutes.

A new design is now being used for the heat transfer gauges which determine the times of arrival of the shock wave at several stations along the tube. These new gauges have been used continuously throughout a series of more than thirty runs extending over a period of a month and their performance has been excellent so far. It still remains to be seen whether they will be able to survive the baking procedure.

Following the completion of the series of experiments using 1% hydrogen in argon, the catalytic effect of oxygen on the dissociation reaction will be studied by measuring the rate of dissociation when known small amounts of oxygen are added to the test gas.

- 6. REFERENCES
- Lordi, J.A. and Mates, R.E., Catalysis of Hydrogen-Atom Recombination in Rocket Nozzles. CAL Report No. AD-1685-A-5 (July 1965)
- 2. Lordi, J.A. Mates, R.E., and Moselle, J.R., Computer Program for the Numerical Solution of Nonequilibrium Expansions of Reacting Mixtures. (In preparation)
- 3. Hurle, I. R. and Russo, A. L., Spectrum Line-Reversal Measurements of Free-Electron and Coupled N₂ Vibrational Temperatures in Expansion Flows. (Paper submitted for publication in J. Chem. Phys.)
- 4. Russo, A. L., Importance of Impurities on Vibrational Relaxation Measurements in N2. (Technical note submitted for publication in J. Chem. Phys.)
- 5. Russo, A. L., Hall, J. G., and Lordi, J. A., Measurements of Non-equilibrium Static Pressures in Nozzle Flows of Dissociated Hydrogen.

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- 6. Russo, A. L., Hall, J. G., and Lordi, J. A., Experimental Studies of Chemical Nonequilibrium in Hydrogen Nozzle Flows. CAL Report No. AD-1689-A-4 (June 1964)
- 7. Hurle, I. R., Russo, A. L., and Hall, J. G., Spectroscopic Studies of Vibrational Nonequilibrium in Supersonic Nozzle Flows. J. Chem. Phys. 40, 2076 (1964)
- 8. Hooker, W.J. and Millikan, R.C., Shock Tube Study of the Vibrational Relaxation of Carbon Monoxide for the Fundamental and First Overtone. J.Chem. Phys. 38, 214 (1963).